Effects of crystal fields on the ground state of a Ce atom

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The $U\to\infty$ limit of the Anderson model of a magnetic impurity in a metal is considered in the presence of crystalline fields. The Bethe-ansatz equations for the ground state are solved for a Ce ion in a cubic environment; and the valence, the population of the levels, the resistivity, and the magnetic susceptibility are obtained. The quenching of the SU(6) Kondo state to an effective SU(2) or SU(4) Kondo state, as well as the universality of the Coqblin-Schrieffer limit, is discussed.

I. INTRODUCTION

The orbitally degenerate Anderson model in the $U\to\infty$ limit (singly occupied $4f$ level) has been the subject of many recent theoretical papers. In particular, the impurity model has been solved by means of Bethe's ansatz[1] and explicit expressions for the ground-state properties,[2–4] as well as the thermodynamic Bethe-ansatz equations,[5] have been obtained. The only SU(N)-symmetry-breaking mechanism treated so far is a magnetic field in the Coqblin-Schrieffer limit.[6]

It is the purpose of this letter to discuss the effect of crystal fields on ground-state properties of the model. Our starting point is the results of Refs. 2–4, which are briefly summarized and discussed in the context of an arbitrary breaking of the SU(N) symmetry. The case of a Ce ion ($j=\frac{5}{2}$) in a cubic environment is then solved explicitly. Crystal fields are usually comparable to the f-level width and sometimes much larger than the Kondo temperature. They are hence an essential feature in a realistic description of Ce systems. Finally, we discuss the Wilson number, which characterizes the universality of the Coqblin-Schrieffer limit.

The model[1–4] consists of a localized f level of degeneracy $N=2j+1$ and energy ϵ, which may be empty or singly occupied, and is hybridized with the conduction electron states through a contact potential V. For a linear dispersion of the conduction states the model is integrable[1] and the Bethe ansatz leads to the following set of integral equations [Eq. (V.8) of Ref. 3]:

$$\left[\tilde{\sigma}^{(l)}(\xi)+\sigma^{(l)}(\xi)+\sum_{q=0}^{2j-1}\int_{-\infty}^{B_q}d\xi'\sigma^{(q)}(\xi')K_{lq}^{j}(\xi-\xi')=\int_{Q}^{\infty}d\xi'\tilde{\sigma}^{(2j)}(\xi')\int_{-\infty}^{\infty}\frac{dx}{2\pi}e^{i(\xi'-\xi)x}\sinh\left[\frac{l+1}{2}x\right]\Big/\sinh\left[\frac{2j+1}{2}x\right]\right.$$
$$\left.+\frac{1}{L}\int_{-\infty}^{\infty}\frac{dx}{2\pi}e^{i(\epsilon-\xi)x}\sinh\left[\frac{2j-l}{2}x\right]\Big/\sinh\left[\frac{2j+1}{2}x\right]\right.$$
$$\text{for } l=0,\ldots,2j-1 \quad (1)$$

and

$$\tilde{\sigma}^{(2j)}(\xi)+\sum_{q=0}^{2j}\int_{-\infty}^{B_q}d\xi'\sigma^{(q)}(\xi')\int_{-\infty}^{\infty}\frac{dx}{2\pi}e^{i(\xi'-\xi)x-j|x|}\sinh\left[\frac{q+1}{2}x\right]\Big/\sinh\left[\frac{x}{2}\right]=\frac{1}{\pi L}\frac{j+\frac{1}{2}}{(\xi-\epsilon)^2+(j+\frac{1}{2})^2}+\frac{2j+1}{2\pi}\ .$$

Here j is the total angular momentum of the f electron, L is the length of the box, and $V^2=2\Gamma=1$, Γ being the resonance width. $\sigma^{(l)}(\xi)$ are density functions of complexes of $(l+1)$ bound (paired) electrons. They consist of an impurity and a host part, $\sigma^{(l)}=\sigma^{(l)}_{\rm host}+(1/L)\sigma^{(l)}_{\rm imp}$. We label the occupation numbers of the levels in decreasing order $n_0\geq n_1\geq\cdots\geq n_{2j}$, such that n_0 corresponds to the lowest-lying level and n_{2j} is the least populated. $\sigma^{(l)}_{\rm host}(\xi)$ is then the density in the electron gas associated with all n_q for $q\leq l$ occupied and $q>l$ empty. The relative occupation of the levels is then given by

$$n_l-n_{l+1}=\int_{-\infty}^{B_l}d\xi\,\sigma^{(l)}_{\rm imp}(\xi),\quad n_{2j+1}\equiv 0\ . \quad (3)$$

In the ground state the density function $\sigma_l(\xi)$ for occupied states vanishes identically for $\xi>B_l$. It is usual to introduce "hole" density functions which are nonvanishing only in the interval $[B_l,\infty]$. The hole functions are denoted $\tilde{\sigma}^{(l)}(\xi)$ and are also given by Eqs. (1) and (2). $Q\equiv B_{2j}$ plays the role of the Fermi level. The explicit form of the kernel K^j_{lq} is given by (V.9) of Ref. 3 and is not needed here. The first term on the right hand side of (1) is the mixed-valence driving term which is responsible for the charge fluctuations. They are suppressed for $Q\to\infty$ and the remaining (second) driving term is the one of the Coqblin-Schrieffer Hamiltonian.

The B_l (including Q) are a set of $N=2j+1$ constants to be determined according to the external conditions imposed on the impurity. They determine the number of electrons of each "color" in the host and, hence, valence

and relative population of the f-level states of the impurity. The splitting of an N-fold multiplet can be expressed as a linear combination of Stevens operators O_l, where $1 \leq l \leq 2j$. In the ionic Hamiltonian there are then $(N-1)$-independent coefficients which uniquely determine the B_l for a fixed Q. The Zeeman splitting, for instance, can be characterized by an O_1 Stevens operator and is the only possible splitting for $j=\frac{1}{2}$. A triplet can in addition be split by an axial crystal field, i.e., an O_2 Stevens operator, etc.

We diagonalize the ionic f-level Hamiltonian and new eigenstates (colors) replace the spin eigenstates. The number of electrons of each color is a conserved quantity of the system (host with impurity) and Eqs. (1)—(3) remain unchanged when reinterpreted in terms of colors. Hence, the splitting scheme of the isolated ion completely determines the one of the interacting system. As a consequence, the Lea, Leask, and Wolf[7] scheme for the level splitting in a cubic environment is valid also in the presence of the Kondo effect. For definiteness, we limit most of our discussion to $j=\frac{5}{2}$, which corresponds to a Ce impurity.

II. ZEEMAN SPLITTING (REF. 6)

We consider a magnetic field and no other symmetry-breaking potentials. The magnetization is given by the superposition of the one induced by the mixed-valence and Kondo driving terms in Eq. (1). Since the resonance width Γ is much larger than any laboratory field, the mixed-valence contribution[2–4] is always linear in H. For the Kondo part, H/T_K is not necessarily a small parameter and a numerical solution of the integral equations is required[6] for $j>1$. The parameters B_l, $l<2j$, are determined such that for small fields $n_l - n_{l+1}$ in Eq. (3) is proportional to H and independent of l. Only one B_l, e.g., B_0, is independent and parametrizes the field; all other B_l differ from B_0 by a constant. Note that from the symmetries of the kernel K^j_{lq} and the driving terms at small fields one has $B_l = B_{2j-l-1}$.

III. AXIAL CRYSTAL FIELD

Let us consider a half-integer j. In the absence of a magnetic field the axial crystalline field splits the N-fold multiplet into $N/2$ Kramers doublets. The two states forming a Kramers doublet are degenerate, i.e., $n_l = n_{l+1}$ or $B_l = -\infty$ for l even. We are then left with $N/2$ coupled integral equations, which yield the $N/2$ occupation numbers of the doublets, i.e., the valence and the $j-\frac{1}{2}$ relative populations. The relative populations are determined by the ionic Hamiltonian, e.g., for Ce, $j-\frac{1}{2}=2$, there is a second- and a fourth-order Stevens operator, for Yb, $j=\frac{7}{2}$, there is in addition a sixth-order Stevens operator. A super-imposed cubic crystal field does not qualitatively change the results.

IV. CUBIC CRYSTAL FIELD

The sixfold multiplet of a Ce ion in a cubic environment splits into a Γ_7 doublet and a Γ_8 quartet. The ionic Hamiltonian consists of only one fourth-order Stevens operator. We denote the splitting with $6b_4$, $b_4>0$ (<0), indicating that the Γ_7 (Γ_8) is the lower-lying level. If $b_4>0$, B_1 and Q are finite, all other $B_l=-\infty$. If $b_4<0$, only B_3 and Q are finite. Equations (1) and (2) then reduce to two coupled integral equations, which for small $|b_4|$ [B_1 (B_3) $\ll Q$] can be solved explicitly, yielding

$$\int d\xi\, \sigma^{(1)}_{\rm imp}(\xi) \Big/ \int d\xi\, \sigma^{(1)}_{\rm host}(\xi) = \chi^s_{\rm imp}/\chi^s_{\rm host}\ , \tag{4}$$

where χ^s is the zero magnetic field susceptibility in the absence of crystal fields [Eq. (V.19) of Ref. 3; note that a factor $(N/2)^{(N-1)/N}$ is missing in that expression]. A similar expression holds for $b_4<0$. Hence, the linear response to a magnetic and a crystal field is the same. The response of a free-electron gas to a crystal field is used to relate B_1 (B_3) to b_4:

$$6|b_4|/\Gamma = (2^{1/3}9/e\pi)\exp[(\pi/6\Gamma)(B-Q)]\ . \tag{5}$$

If $6|b_4|/\Gamma$ is not small, the two coupled integral equations require a numerical solution. The valence, the population difference between Γ_7 and Γ_8, and the resistivity as a function of crystal field splitting are shown in Fig. 1 for

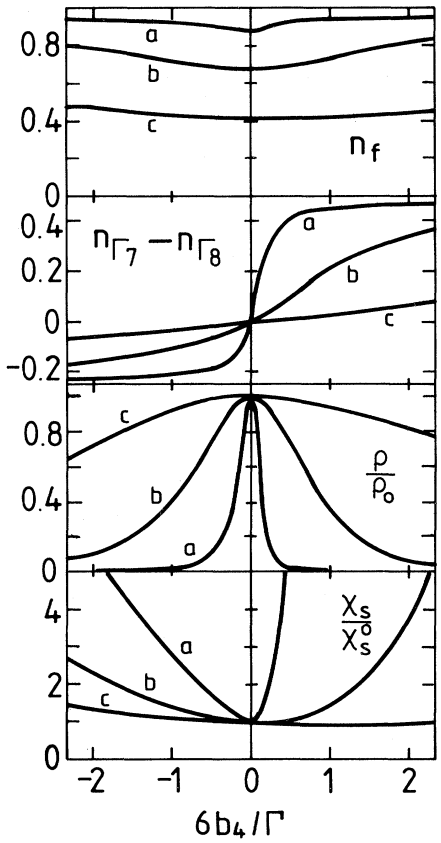

FIG. 1. Mixed-valence Ce ion in a cubic crystal field. The splitting between the Γ_7 and Γ_8 multiplets is $6b_4$. Γ is the resonance width, n_f is the valence, n_{Γ_7}-n_{Γ_8} the difference in level population, ρ/ρ_0 the resistivity normalized to its zero-field value, and χ_s/χ_s^0 the spin susceptibility normalized to its value for $b_4=0$. The curves correspond to (a) $\epsilon-Q=-12\Gamma/\pi$, (b) $\epsilon=Q$, and (c) $\epsilon-Q=12\Gamma/\pi$. The relation to $\tilde{\epsilon}$ of Refs. 2 and 3 is $\tilde{\epsilon}=(\pi/2\Gamma)(\epsilon-Q)-[j-\frac{1}{2}\ln 2-\frac{1}{2}N\ln\frac{1}{2}N)]$.

three f-level positions. Note that the valence grows with the splitting, the growth being proportional to b_4^2 for small fields. (There is no linear change in b_4, since the trace of Stevens operators vanishes.) As expected from Eq. (4), the relevant energy scale for variations of $n_{\Gamma_7}-n_{\Gamma_8}$ is the Kondo temperature of the $j=\frac{5}{2}$ sixtuplet, unless the f level is far above the Fermi energy (strong mixed-valence regime). For large fields, either n_{Γ_8} or n_{Γ_7} gets small and reduces the scattering phase shift, such that the resistivity decreases.

V. CUBIC CRYSTAL FIELD AND SMALL MAGNETIC FIELD

We restrict the discussion to $b_4>0$; the case $b_4<0$ follows analogously. If the magnetic field is small compared with all other energies in the system, it can be treated as a perturbation. This means that $B_0,B_2,B_3,B_4 \ll \epsilon,B_1,Q$. All B_l are finite since all the degeneracies are released. We eliminate $\sigma^{(1)}(\xi)$ in Eq. (1) and express it in terms of its "hole" function $\tilde{\sigma}^{(1)}(\xi)$. The feedback of the magnetic field on $\tilde{\sigma}^{(1)}(\xi)$ and $\tilde{\sigma}^{(5)}(\xi)$ is of higher order than linear response and is neglected. The equations for $\sigma^{(1)}(\xi)$ and $\sigma^{(5)}(\xi)$ then decouple from the other four and the results of Sec. IV can be used. The driving terms of the remaining four equations depend now on $\tilde{\sigma}^{(1)}(\xi)$ and $\tilde{\sigma}^{(5)}(\xi)$. Note that the elimination of $\sigma^{(1)}$ in (1) has modified the kernel of the integral equations. The new kernel completely decouples $\sigma^{(0)}(\xi)$ from $\sigma^{(l)}(\xi)$, $l=2,3,4$. The kernel for the $\sigma^{(0)}$ equation is the one of a spin-$\frac{1}{2}$ and this equation describes the Zeeman splitting of the Γ_7. The kernel of the other three integral equations corresponds to a $j=\frac{3}{2}$ and is identified with the Γ_8 multiplet.

In a small magnetic field the system behaves like a Fermi liquid, such that the solutions for the impurity and the host are proportional. Since the susceptibilities in the free-electron gas are known, it is not necessary to actually solve the equations. The impurity spin susceptibility is given by $\chi_s=\chi_{\Gamma_7}+\chi_{\Gamma_8}+\chi_{vv}$, the latter term being the van Vleck susceptibility:

$$\chi_{\Gamma_7}=\frac{25}{36\pi}\left[\exp\left[\frac{\pi}{2\Gamma}(B_1-\epsilon)\right]+2\pi\tilde{\sigma}^{(1)}_{\rm imp}(i\pi)\right]\Big/2\pi\hat{\tilde{\sigma}}^{(1)}_{\rm host}(i\pi)\ , \tag{6}$$

$$\chi_{\Gamma_8}=\frac{65}{18\pi}\left[\hat{\tilde{\sigma}}^{(1)}_{\rm imp}\left[i\frac{\pi}{2}\right]+\hat{\tilde{\sigma}}^{(5)}_{\rm imp}\left[i\frac{\pi}{2}\right]\exp\left[\frac{\pi}{4\Gamma}(B_1-Q)\right]\right]\left[\hat{\tilde{\sigma}}^{(1)}_{\rm host}\left[i\frac{\pi}{2}\right]+\hat{\tilde{\sigma}}^{(5)}_{\rm host}\left[i\frac{\pi}{2}\right]\exp\left[\frac{\pi}{4\Gamma}(B_1-Q)\right]\right]^{-1}\ , \tag{7}$$

$$\chi_{vv}=\tfrac{40}{27}2\pi\hat{\sigma}^{(1)}_{\rm imp}(0)/b_4\ , \tag{8}$$

where $\hat{\sigma}$ denotes the Fourier transform of σ.

For small crystal fields only the $\hat{\tilde{\sigma}}^{(1)}$ contributions are relevant and one recovers the susceptibility of the isotropic SU(6) impurity. For large b_4, $\hat{\tilde{\sigma}}^{(1)}$ plays a secondary role, and the main contribution comes from the exponential in (6). This term represents the Kondo susceptibility of the Γ_7 doublet. Note that $\hat{\tilde{\sigma}}^{(1)}_{\rm host}$ is essentially linear in b_4, such that the Kondo temperature depends on b_4 like

$$T_K^{\Gamma_7}\sim(\epsilon_F^2/b_4^2)\exp[(\pi/2\Gamma)(\epsilon-\epsilon_F)]\ .$$

This result has also been obtained through renormalization-group arguments. If $b_4<0$, the Kondo term appears in χ_{Γ_8} and the Kondo temperature has, asymptotically for $T_k \ll |b_4| \ll \Gamma$, the form

$$T_K^{\Gamma_8}\sim\epsilon_F(\epsilon_F/|b_4|)^{1/2}\exp[(\pi/4\Gamma)(\epsilon-\epsilon_F)]\ .$$

The susceptibility as a function of b_4, normalized to its $b_4=0$ value, is shown in Fig. 1.

VI. UNIVERSALITY OF THE COQBLIN-SCHRIEFFER LIMIT

In the Kondo limit the magnetization and the population difference between the Γ_7 and Γ_8 levels are universal functions of H/T_K and b_4/T_K, respectively. The universality is characterized by the Wilson number[8] that relates the low- and high-temperature response to a small field. The Wilson number is independent of the mechanism lifting the N-fold degeneracy, e.g., crystal or magnetic field,

$$W=2\beta\gamma\exp\left[-\frac{3}{2}\left[1+\frac{1}{N}\right]\right]\Big/\Gamma\left[1+\frac{1}{N}\right]\ , \tag{9}$$

where γ is Euler's constant and $\beta=1.938\,90$. Expression (9) contains the known cases $N=2$ (Ref. 9) and $N=3$ (Ref. 10) and agrees with the numerical values[11] for $j>1$. The Wilson numbers obtained in Ref. 12 are not correct.

In summary, we solved the Bethe-ansatz equations for the ground state of a Ce ion in a cubic crystal field and showed the quenching of the SU(6) Kondo ground state with growing field into an effective SU(2) or SU(4) Kondo state. Extensions to other systems and symmetries are now straightforward. In view of the experimental importance of crystal fields, we believe this result is a relevant step toward a realistic description of impurity systems.

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